

Photoinduced absorption from localized intra-gap states.

V.V. Kabanov^a, J. Demsar^a and D. Mihailovic^a

^aJosef Stefan Institute 1001, Ljubljana, Slovenia.

A model is developed for photoinduced absorption from localized states observed in femtosecond pump-probe experiments in high- T_c superconductors and other materials. The dynamics of localized carriers are described in terms of phenomenological approach similar to that originally proposed by Rothwarf and Taylor. Expanding the relaxation rate in powers of the order parameter we have shown that density of localized carriers is sensitive to T_c . From the analysis of the experimental data on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{K}_{0.3}\text{MoO}_3$ we conclude that significant intra-gap density of localized states exists in these materials. Temperature dependence of the density of photoexcited localized carriers in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and in $\text{K}_{0.3}\text{MoO}_3$ is consistent with the observation of the pseudogap above T_c .

1. Introduction

Recent pump-probe experiments on cuprate superconductors [1–4] and some other materials [5] have shown that a photoinduced change in absorption or reflection can be observed at low temperatures and especially for $T < T_c$. The effects are believed to be caused by excited state absorption of the probe pulse from photoexcited quasiparticle (QP) states [4] and theoretical analysis of the response was found to be in good agreement with experimental data on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ over a wide range of doping [4]. However, in addition to the QP response which occurs on the picosecond and subpicosecond timescale, a distinct slower response was also consistently observed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) [2], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BISCO) and $\text{Bi}_2\text{Y}_x\text{Ca}_{1-x}\text{SrCu}_2\text{O}_8$ [6] and more recently in the charge-density-wave (CDW) quasi one-dimensional Peierls insulator $\text{K}_{0.3}\text{MoO}_3$ [5]. It was shown to be of non-thermal origin (detailed analysis is given in Ref. [6]) and occurs on a timescale of 10^{-8} s or longer. Its anomalous T -dependence in the two systems [2,5] lead the authors to the suggestion that the signal is due to localized states near the Fermi energy.

In semiconductors in-gap localized states lead to a photoconductivity effect due to reduced relaxation rate of one of the PE carriers. Photoconductivity was indeed observed in underdoped

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [7]. With increase of the level of doping it is difficult to detect small photoconductivity because of the increase of the dark conductivity. The observation of long-lived component in photoinduced change of absorption is more effective way to detect in-gap localized states because optical conductivity in the range of charge transfer gap shows relatively small changes with increase of doping.

2. Theoretical model

As photons from the pump laser pulse are absorbed, they excite electrons and holes with the energy scale of the order of the photon energy. These particles release their extra kinetic energy by electron-electron scattering. When electrons reduce their energy to the value of the order of phonon frequencies electron-phonon scattering becomes dominant. This energy relaxation process is very rapid and the particles end up in QP states near the Fermi energy within $\tau_e = 10 \sim 100$ fs [4]. Subsequent relaxation is slowed down by the presence of the gap and a relaxation bottleneck is formed. From pump-probe photoinduced transmission experiments in YBCO [1,4] and BISCO [6], the relaxation times of the photoexcited QPs were found to be in the range $\tau_{QP} = 0.3 \sim 3$ ps. It is important that value of the gap in high- T_c materials is of the order of phonon

frequencies, therefore electron-phonon scattering is dominant only in recombination of electrons through the gap.

In addition to the picosecond transient, the signal on nanosecond timescale has been consistently observed in HTSC [2,6] and recently also in the quasi 1D CDW insulator $K_{0.3}MoO_3$ [5]. After photoexcitation the signal relaxes within 10 ps to some non-zero value, that can be represented by a constant on the 100 ps timescale [6]. The lifetime of the slow component, τ_L , cannot be directly measured, since it appears to be longer than the inter-pulse separation of $t_r \simeq 10 - 12$ ns. This results in a signal pile-up due to accumulation of the response from many pulses (presence of photo-induced signal at negative time-delay). From the experiments [2,5] it appears that $\tau_L > 10^{-7}$ s. This is long in comparison with the phonon relaxation time and with the phonon escape time from the excitation volume into the bulk or thin film substrate, which is typically 10^{-10} s, so we can ignore phonon escape effects and discuss only intrinsic relaxation processes.

Since the relaxation time τ_L is long in comparison with τ_{QP} and phonon relaxation times, we assume that phonons and quasiparticles can be described by equilibrium densities N_ω and N respectively. For the relaxation of the localized carriers we apply arguments similar to those originally proposed by Rothwarf and Taylor [8]. The rate equation for the total density of localized excitations N_L is then given by:

$$\frac{dN_L}{dt} = -RN_L^2 - \tilde{\gamma}N_L + \gamma N + \beta N_\omega. \quad (1)$$

The first term in Eq.(1) describes the recombination of two localized excitations to a condensate with a recombination rate R . The second and the third terms describe the exchange of an electron or a hole between the localized and quasiparticle states with densities N_L and N respectively and with a rates $\tilde{\gamma}/\gamma \propto \exp(-\Delta E/k_B T)$ where ΔE is the energy barrier between trapped carriers and quasiparticles [9]. The last term describes the spontaneous creation of localized excitations by phonons with a relaxation rate β . When electron or hole is trapped additional contribution to the energy barrier may appear due to a local lat-

tice distortion (polaronic effect). We assume that the energy barrier does not depend on whether localized state is occupied or not.

Assuming the ansatz for $N_L = N_{L0} + n_L$, where N_{L0} is equilibrium density of localized particles and n_L is the photoinduced density created by the laser pulse and taking into account that N_ω and N are given by their equilibrium values, we can rewrite Eq.(1):

$$\frac{dn_L}{dt} = -Rn_L^2 - (2RN_{L0} + \tilde{\gamma})n_L \quad (2)$$

This equation is sufficiently general that it can be applied to different systems with different types of ground states. The analytic solution of Eq.(2) has the form:

$$n_L(t) = \frac{n_L(0)}{\left(1 + \frac{n_L(0)}{\tau}\right) \exp(t/\tau) - \frac{n_L(0)R}{\tau}}. \quad (3)$$

where $1/\tau = 2N_{L0}R + \tilde{\gamma}$. Since we are interested in a steady state solution for the case of excitation by repetitive pump pulse train, we use the condition that total number of localized excitations that recombine between two laser pulses should be equal to the number of localized excitations created by each laser pulse.

$$n_L(0) - n_L(t_r) = \eta n_{QP}. \quad (4)$$

Here n_{QP} is the number of photoinduced quasiparticles created by each laser pulse [4], $\eta \propto \gamma \tau_{ph}$ is the probability of trapping a photoinduced carrier into a localized state, $\tau_{ph} \propto 1/\Delta(T)$ is quasiparticle relaxation time. Combining Eqs.(3) and (4) one obtains the stationary solution for $n_L(0)$:

$$n_L(0) = \left[\sqrt{1 + \frac{\eta n_{QP}}{N_{L0}/2\tau t_r}} - 1 \right] / 2\tau R$$

3. Results

In the line with Ginzburg-Landau approach we can expand recombination rate R in even powers of order parameter:

$$R = \Gamma + \alpha \Delta(T)^2 + \dots \quad (5)$$

In the BCS-like case pairing occurs at T_c and biparticle recombination is impossible above T_c ($\Gamma = 0$). This result is consistent with calculations of QP recombination rates[10]. In the case

of preformed pairing the first term in Eq.(6) is not 0 and biparticle recombination is possible above T_c .

This simple observation makes temperature dependence of the amplitude of slow component very different in these two cases [11]. In the case of BCS-like pairing, the recombination rate is large at low temperature. It leads to a small amplitude of the photoinduced signal. With increase of T , the recombination rate decreases and relaxation via thermally activated QP is dominant. As a result, a sharp maximum in the amplitude of the photoinduced signal is observed near T_c [11]. In the case of preformed pairing, a similar increase of the amplitude takes place below T_c . Since Γ is finite, the amplitude of the signal is a smooth function above T_c [11].

To compare the theory (Eqs.(5,6)) with experiments we have plotted experimental data for overdoped $\text{Ca}_{0.132}\text{Y}_{0.868}\text{Ba}_2\text{Cu}_3\text{O}_{6.928}$ (Fig.1a), for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Fig.1 b) and for CDW insulator $\text{K}_{0.3}\text{MoO}_3$ (Fig.2) samples. As clearly seen from the fit theory provides qualitative and some time quantitative description of the observed photoinduced changes of the absorption. In the case of overdoped $\text{Ca}_{0.132}\text{Y}_{0.868}\text{Ba}_2\text{Cu}_3\text{O}_{6.928}$ (Fig.1a) a signal has been detected above T_c . This observation is consistent with existence of pseudogap above T_c [3] and supports the statement that overdoped materials are spatially inhomogeneous. In the case of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Fig.1 b) the theory provides an accurate description of the data. The existence of a pseudogap is clearly seen well above T_c .

The non-bolometric long-lived signal exists above T_c in the case of CDW insulator $\text{K}_{0.3}\text{MoO}_3$ (Fig.2) as well. This could be attributed to the presence of pseudogap in the density of states due to a locally formed gap. This is consistent with earlier measurements on $\text{K}_{0.3}\text{MoO}_3$ [12] that show a decrease of the density of states above T_c . In all cases the parameters used in the fits are the same as used in the analysis of QP relaxation [4,5]. At low temperature there is a deviation of the calculated curves from the experimental points. To explain this effect we note that Eq.(6) is valid near T_c where Δ is small. Higher order terms in

the expansion of R can explain this deviation.

4. Discussion

In cuprate superconductors there is spectroscopic evidence suggesting that there is a significant density of states in the gap possibly extending to the Fermi level, which is often attributed to a d -wave gap symmetry. However, by normal spectroscopies it is difficult to determine if the states in the gap are QP states or, for example, localized states. Time-resolved spectroscopy can answer this question rather effectively because of the different time- and temperature-dependences of the QP and localized carrier relaxations. It was argued that in the presence of impurity scattering QP DOS in the d -wave state remains finite at zero energy [13]. Recently it was proposed [14] that the quasiparticles in the superconducting state may become localized for short coherence length d -wave superconductors. On the basis of available experimental data we cannot make any definite conclusion about the *origin* of intra-gap localized states. However preliminary data on electron irradiated samples show only weak dependence of the amplitude of the signal on the irradiation flux. It is inconsistent with a simple d -wave interpretation of localized states where an exponential dependence of the density of states on impurity concentration is expected [13].

We can, however estimate the density of the intra-gap states from the available data by assuming that the optical probe process is similar for excited state absorption from localized states and for QPs. From typical photoinduced reflection data for YBCO, we find that the amplitude of signal associated with QP response is approximately equal to the amplitude of the long-lived signal. It implies that also $n_L(0) \simeq n_{QP}$. From this we can conclude that the density of intra-gap states is comparable with the density of QP states. This observation has important implications for the interpretation of frequency-domain spectroscopies, since it suggests that the spectra should show a very significant intra-gap spectral density due to localized states, irrespective of the gap symmetry.

In conclusion, we mention some of the most

likely possibilities of the origin of the localized states: (i) localized states associated with the inhomogeneous ground state of the cuprates (stripes) [15], (ii) intrinsic defect states, (iii) localized QP states in d -wave superconductor [14]. In $K_{0.3}MoO_3$, the nature intra-gap excitations has been a subject of extensive study over the years and the reader is referred to ref. [12] for a review. However, the fact that the signals in $K_{0.3}MoO_3$ and $YBa_2Cu_3O_{7-\delta}$ are very similar appears to rule out both spin excitations and vortex states, leaving localized charges as the most plausible origin of the intra-gap states.

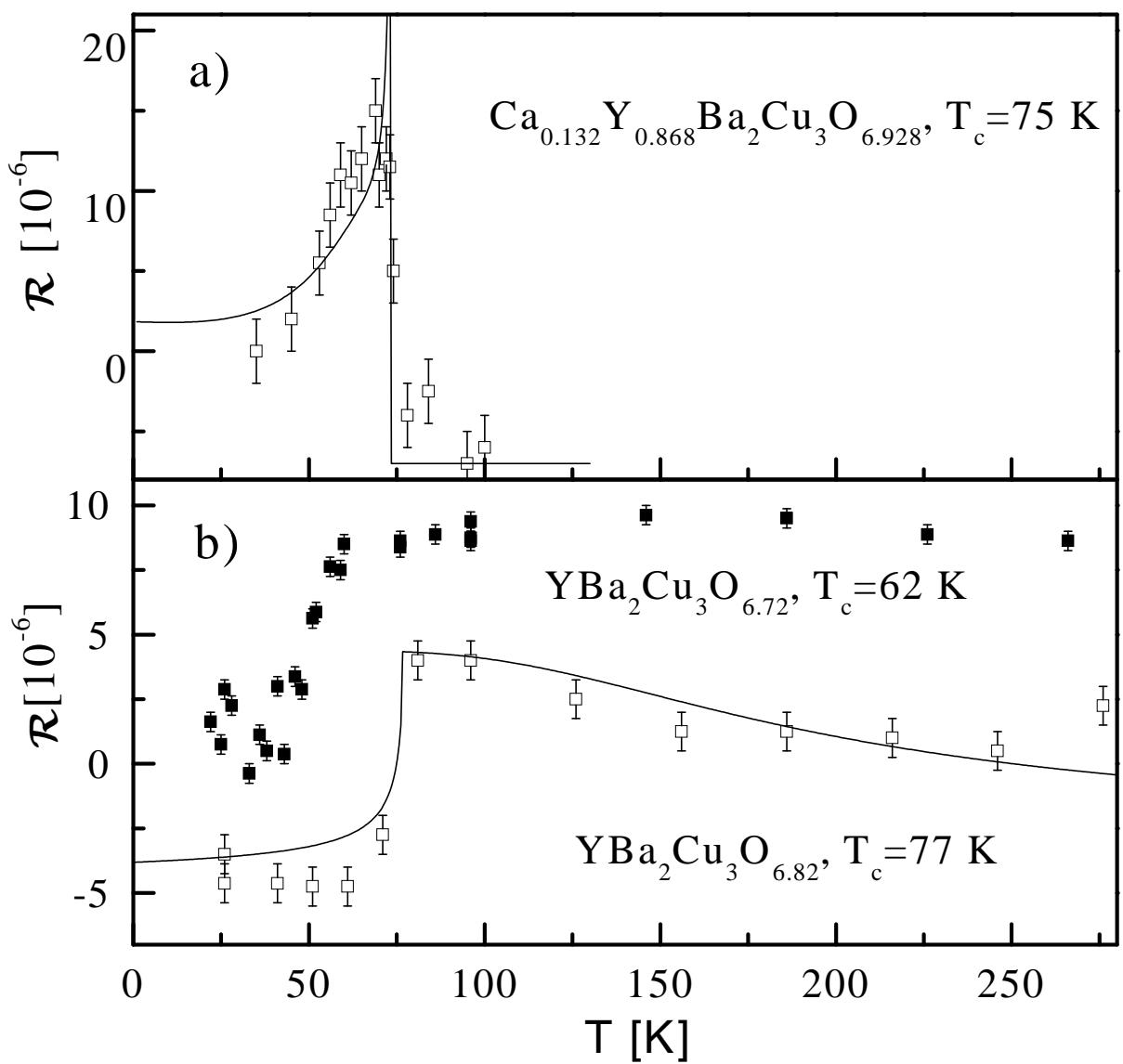
5. Figure Captions

Figure 1: T-dependence of ns component amplitude \mathcal{R} in a) Ca overdoped YBCO and b) underdoped YBCO, together with the fits.

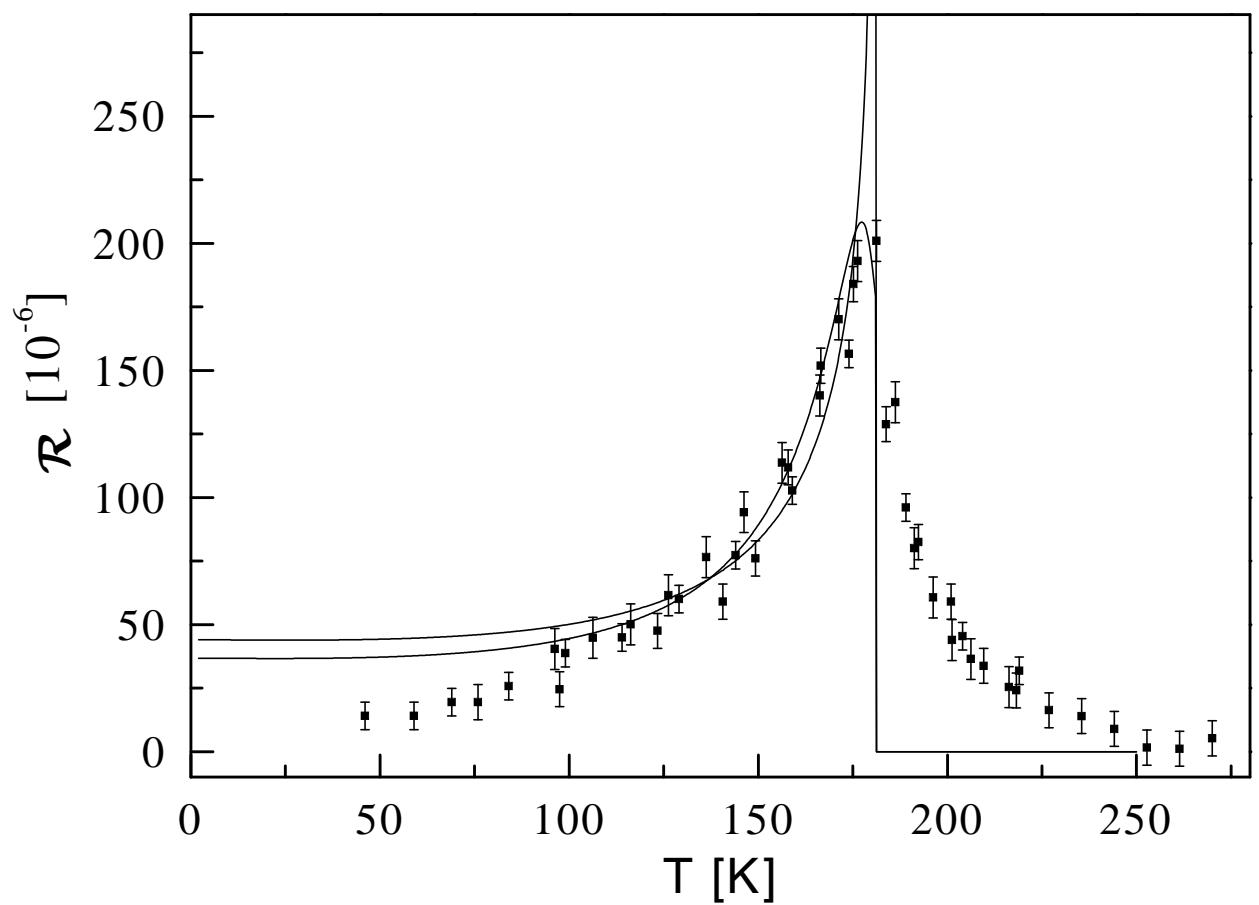
Figure 2: T-dependence of ns component amplitude \mathcal{R} , taken on $K_{0.3}MoO_3$ ($T_c = 183$ K) together with the fit using BCS-like gap.

REFERENCES

1. S.G.Han et al., Phys.Rev.Lett. **65**, 2708 (1990).
2. C.J.Stevens et al, Phys. Rev. Lett., **78**, 2212 (1997).
3. J.Demšar et al., Phys.Rev.Lett. **82**, 4918 (1999).
4. V.V. Kabanov et al, Phys. Rev. B, **59**, 1497 (1999).
5. J.Demšar, D.Mihailovic and K.Biljaković, Phys.Rev.Lett., **83**, 800 (1999).
6. T.N.Thomas et al, Phys.Rev.B, **53**, 12436 (1996).
7. G. Yu, et al Phys. Rev. B **48**, 7545 (1993).
8. A. Rothwarf and B.N. Taylor, Phys. Rev. Lett., **19**, 27 (1967).
9. S.M. Ryvkin, *Photoelectric Effects in Semiconductors*, Consultants Bureau, NY, (1964).
10. Yu. N. Ovchinnikov and V.Z. Kresin, Phys. Rev. B **58**, 12416 (1998).
11. V.V. Kabanov, J. Demšar, D. Mihailovic, Phys. Rev. B, **60**, 1477 (2000).
12. See G.Grüner, *Density Waves in Solids*, (Addison-Wesley, 1994).
13. L.P. Gorkov and P.A. Kalugin, *Pis'ma Zh. Eksp. Teor. Fiz.* **41**, 208 (1985).[*JETP lett.* **41**, 253 (1985)].
14. P.A. Lee, *Phys. Rev. Lett.* **71**, 1887 (1993)
15. D.Mihailovic and K.A.Müller, in "High- T_c Superconductivity 1996: Ten years after the discovery" (NATO ASI Series E: Applied Sciences, vol. 343) Eds. E.Kaldis, E.Liarokapis and K.A.Müller (Dordrecht:Kluwer 1997) p.243.



Kabanov et al., Fig. 1



Kabanov et al., Fig.2